

## Conference Paper

# Production of Synthetic Wollastonite Using Gypsum Technogenic Raw Materials

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## Abstract

The paper analyzes the literature in the field of synthetic wollastonite production using gypsum technogenic raw materials. Using the example of the complex processing of boric acid production wastes the possibility of obtaining synthetic wollastonite at different modes of waste processing is shown. Possible areas of the practical application of the obtained wollastonite are analyzed.

**Keywords:** gypsum technogenic raw materials, borogypsum, wollastonite, technogenic waste, concrete fillers, polymeric composite materials.

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## 1. Introduction

The economic capacity of the Russian Federation is largely determined by its mineral reserves. Non-renewability and deficiency of mineral raw materials, the current extensive strategy of their extraction and processing contribute to the exacerbation of problems its rational use [1].

Involvement of industrial waste in the economic turnover as a secondary mineral resource represents a perspective in solving the problem while fulfilling the resource-saving and nature environmental function. As the reserves of the developed deposits are depleted for numerous mining and metallurgical enterprises technogenic objects can become a priority and in some cases the only source of mineral raw materials [2].

The problem of using multi-tonnage gypsum-containing technogenic waste generated as a result of the chemical, food and other industries activities (e.g., phosphogypsum, borogypsum, chlorogypsum, ferrogypsum, titanium gypsum) is of practical interest. More than 50 types of gypsum-containing wastes are known, and considerable experience of their use has been accumulated, in particular, in the production of gypsum building materials. The potential use of gypsum waste and the production of a wide range of different materials are being actively considered by many researchers.

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An interesting direction of using gypsum technogenic waste is the production of calcium silicates, which are widely applied in the production of building materials, paper, paints, plastics, composite polymeric and metal-ceramic materials, sorbents for water purification [3]. Of particular practical interest is the  $\text{CaSiO}_3$  wollastonite, whose important technological properties are high chemical resistance in various environments, low specific weight, unique dielectric properties, and low thermal conductivity, as well as environmental purity and safety [4, 5]. Wollastonite market review performed by the research group "Infomine" is noted that China, India, and the USA currently are the top three leaders in the production of wollastonite [6]. Despite the existing demand of many domestic industries and the availability of explored deposits of mineral extraction the Russian Federation is almost practically not involved in development in the direction of wollastonite production.

Same time in addition to natural deposits of wollastonite in Russia there is a large number of so-called "technogenic deposits", which are a promising source of raw materials for the production of synthetic wollastonite, including gypsum man-made waste (phosphogypsum, borogypsum).

Currently, there are many ways to obtain wollastonite from various calcium-containing and silicon-containing compounds: molten methods of wollastonite obtaining, hydrothermal (autoclave) synthesis of calcium hydrosilicates with subsequent firing, the synthesis by direct solid-phase reactions at elevated temperatures. The low-temperature non-autoclave synthesis of calcium silicates based on the interaction of initial components in an aquatic environment is noted as the most promising way of their production. Thus, the paper [7] suggests a method of obtaining wollastonite from phosphogypsum, silicon dioxide, and coke by reducing of phosphogypsum charge at a temperature of 1200 °C. The method intensifies and simplifies the process of wollastonite obtaining. Besides, the use of phosphogypsum makes possible to obtain sulfur dioxide gas for the production of sulphuric acid.

The paper [8] suggests a method of wollastonite obtaining by melting phosphogypsum and silica gel (waste of aluminum fluoride production) or quartz sand in the presence of sulfur, carbon, zinc sulfate and calcium phosphate at a temperature of 1250–1300 °C; followed by a sharp cooling of the melt in water and subsequent processing of granules in an oxidizing medium at 830–920 °C. The proposed method allows to obtain needle-type wollastonite with the ratio  $l/d > 30$  and recovery of 96–97 %.

In the 1980s, the authors [9] proposed technology for processing borogypsum to produce wollastonite and sulfur dioxide. The proposed method includes heat treatment of borogypsum by direct electric heating at 1250–1300 °C for 25–30 minutes, cooling of the resulting melt at the rate of 3–5 °/min and capture of sulfur dioxide.

Scientists from Tunisia [10] proposed a low-temperature method of obtaining calcium silicate and sodium sulfate from phosphogypsum. It has been established that the optimal degree of reaction (98 %) is achieved by adding a pre-prepared solution of sodium silicate ( $\text{SiO}_2 / \text{Na}_2\text{O}=1$ ) to an aqueous suspension of phosphogypsum (optimal solid:liquid ratio 1:12) with subsequent mixing for 60 min. It is shown that as a result of sludge roasting at 900 °C, obtained as a result of the reaction, the formation of wollastonite takes place.

A similar method was previously proposed by Romanian scientists [11]. Xonotlite  $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})$  formed as an intermediate product of the interaction between sodium metasilicate and phosphogypsum (or natural gypsum) after being drying and then fired at 800 °C for 15 min forms  $\beta$ -wollastonite. Sodium sulfate  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is crystallized from the filtrate.

At the Institute of Technology named of N.M. Bardygin (Yegoryevsk, Russia) Moscow State Technological University “Stankin” (MSTU Stankin) developed a technology of low-temperature hydrochemical synthesis of calcium hydrosilicates and fine wollastonite from technogenic waste (phosphogypsum and silica gel) in the presence of metal hydroxides of I and II groups, ammonium or their mixtures and sodium chloride [12–14]. The method allows to produce wollastonite of high purity, whiteness, and homogeneity of particle size (75–85 % of powders consist of 3–12 microns particles), to dispose of wastes from the production of phosphate fertilizers and aluminum fluoride, to simplify and reduce the cost of the process [12].

Since 2007, the Institute of Chemistry of the Far Eastern Branch of the Russian Academy of Sciences in cooperation with the Vladivostok State University of Economics and Service and the Far Eastern Federal University have been actively involved in the development of the physical and chemical basis for the complex processing of multi-tonnage boric acid production wastes (borogypsum) accumulated in the Far Eastern Federal District (Dalnegorsk and Komsomolsk-on-Amur). The possibility of complex processing of borogypsum with the production of calcium silicates, including wollastonite, and potash fertilizers has been shown [15–19]. The authors of this paper present the main results of experimental works on obtaining calcium and wollastonite hydrosilicates from borogypsum and research for potential areas of their practical application.

## 2. The Experimental Part

## 2.1. Characteristics of borogypsum

The decomposition of datolite concentrate with sulphuric acid is accompanied by the formation of a solid waste containing  $B_2O_3$  0.9–2.2 mass. %, which is why this sludge is called borogypsum. The main components of borogypsum are calcium sulfate dihydrate and amorphous silica. For the ton of produced boric acid there is up to 5–5.5 tons of borogypsum.

According to gamma-spectrometric analysis, the calculated specific effective activity of natural radionuclides ( $^{40}K$ ,  $^{226}Ra$ ,  $^{232}Th$ ) for borogypsum waste is 17.9 Bq/kg, which allows the material to be used for the production of all types of building materials.

Borogypsum is characterized by the following content of main components, mass. %:  $SiO_2$  – 26–28;  $CaO$  – 26–28;  $SO_4^{2-}$  – 38–40;  $Fe_2O_3$  – 1.8–2;  $Al_2O_3$  – 0.6–0.8;  $B_2O_3$  – 0.7–1.2;  $MnO$  – 0.2;  $MgO$  – 0.1–0.2.

Borogypsum is of particular interest due to it contains both calcium and silicon components (calcium sulfate dihydrate and amorphous silica) in an optimal ratio to produce wollastonite, and therefore does not require raw materials from additional sources for additional charging of the initial mixture.

## 2.2. Synthesis of wollastonite

The initial components (borogypsum and potassium hydroxide) were mixed in a stoichiometric ratio during different time intervals. Waste treatment temperature, °C: normal conditions (mixing and ultrasonic treatment) — 20–95; microwave treatment — 95; autoclave treatment — 120–220. Depending on the treatment mode, the synthesis was performed by mixing on a laboratory shaker, in an ultrasonic sink, in a microwave oven or in an autoclave. After the end of the set time interval the resulting mixture was removed from the reaction vessel. The sludge was separated from the solution by filtration through a paper filter "blue tape", washed with distilled water, heated to 60–70 °C, and dried at 85 °C for 5 hours. The extent of the reaction was controlled by the residual concentration of potassium hydroxide in solution. To obtain wollastonite, the sludge after synthesis was firing in the temperature range of 900–1000 °C for 1 hour.

## 2.3. Analysis methods

Phase identification of the precipitates was carried out by the X-ray diffraction analysis (XRD) using a D8 Advance diffractometer (Bruker AXS, Germany).

Images of the investigated samples microstructure were obtained via scanning electron microscopy (SEM) using an S-5500S device (Hitachi, Japan) with the Thermo Scientific's energy dispersion analysis attachment.

Bending and compression testing of specimens carried out on a combined machine (Testing, type 1.0244). Concrete samples were tested for water absorption and frost resistance according to the methods described in GOST 12730.3-78 and GOST 10060-2012.

To obtain polymeric composite materials (PCM) based on ultra-high molecular weight polyethylene (UHMWPE) with the addition of wollastonite, as a polymeric matrix the GUR-4022 (Celanese, China) was used. The GUR-4022 properties: molecular weight  $5.3 \times 10^6$  g/mol, average particle size 145 microns and density  $0.93 \text{ g/cm}^3$ .

Physical and mechanical properties of UHMWPE and PCM were studied on the Auto-graph AGS-J tension testing machine (Shimadzu, Japan). Tensile strength, yield strength and relative elongation were carried out according to GOST 11262. The tribotechnical characteristics of UHMWPE and PCM were determined by the UMT-3 universal testing machine (CETR, USA). The friction coefficient was determined according to GOST 11629.

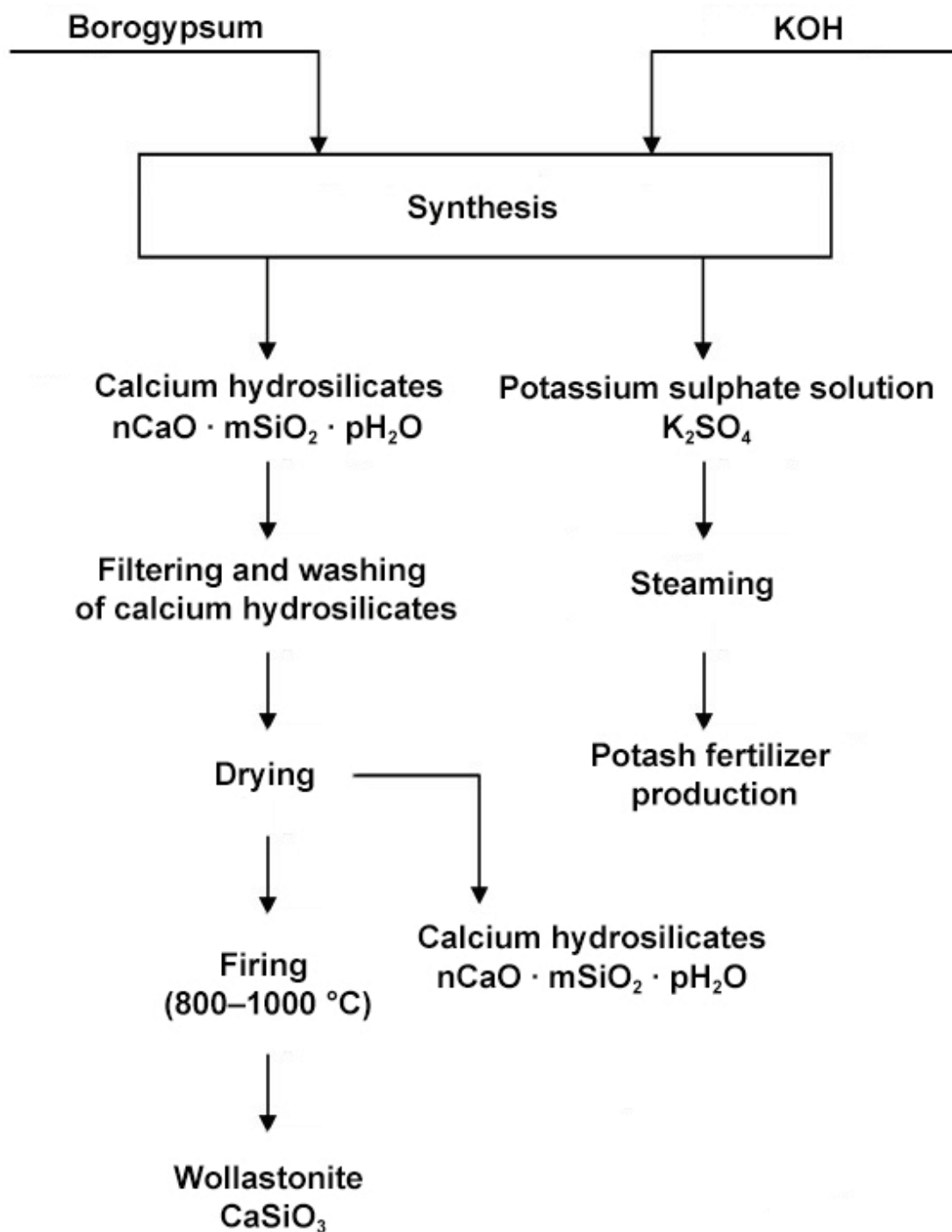
### 3. Results and Discussion

Process flow diagram for calcium hydrosilicates, wollastonite and potassium fertilizers production using borogypsum is presented in Figure 1.

The results from the study of temperature influence on the kinetics of calcium and wollastonite hydrosilicates formation [20–22] shown that microwave and autoclave treatment contribute to increasing the yield of the target product (wollastonite) up to 90–99 % (Figure 2).

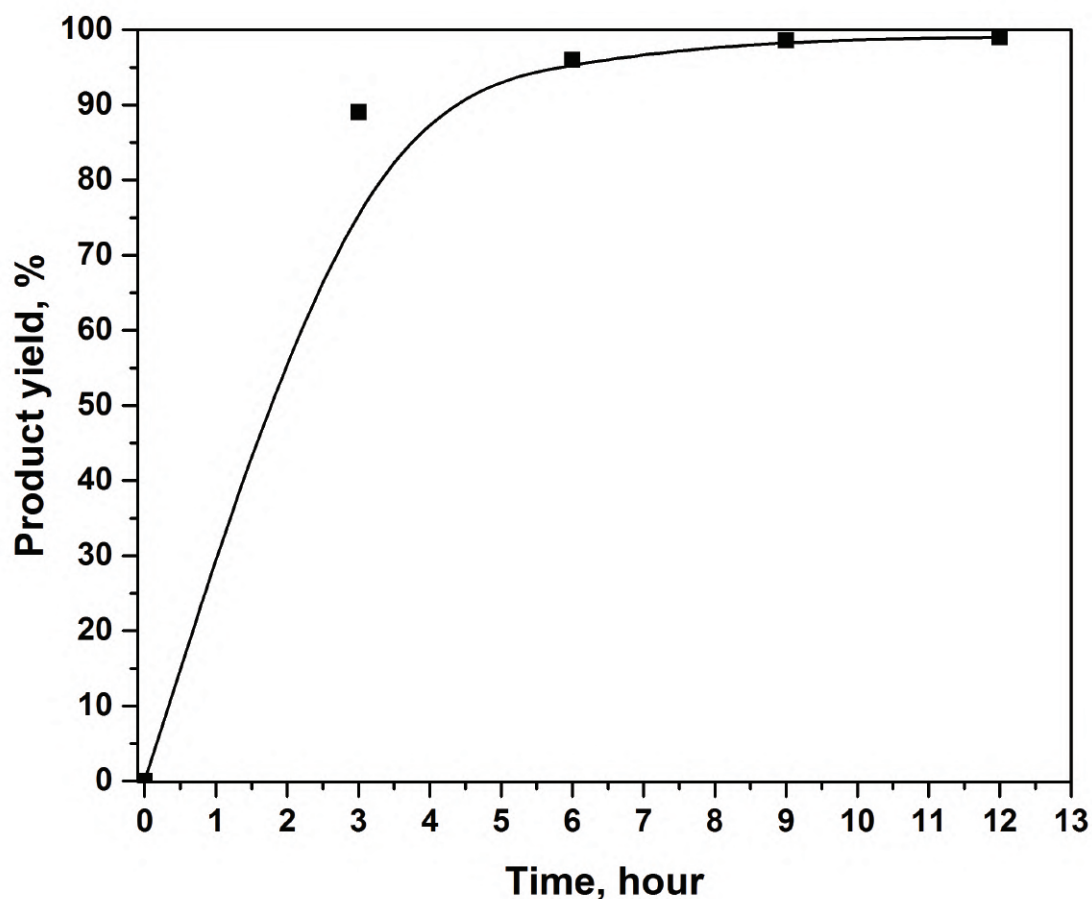
It was shown that as a result of borogypsum autoclave treatment at  $220^\circ\text{C}$ , the formation of triclinic wollastonite (with the crystal cell parameters:  $a=7.92580$ ;  $b=7.32020$ ;  $c=7.06530$ ;  $\alpha=90.055$ ;  $\beta=95.217$ ;  $\gamma=103.426$ ) with the needle form of particles (Figure 3) occurs [23]. It is known that the needle form of wollastonite grain determines its main direction of use as a micro reinforcing filler in various composite materials [24, 25].

The authors have established that wollastonite and additives based on it obtained under autoclave treatment conditions are promising for their application in the construction industry, for example, in fine-grained concrete [26, 27]. The obtained results have shown that the addition of material based on wollastonite, produced by autoclave synthesis from borogypsum, increases the strength, reduces water absorption and increases the frost resistance of concrete (Figure 4 and 5).



**Figure 1:** Process flow diagram for calcium hydrosilicate, wollastonite and potassium fertilizers production using borogypsum [15]

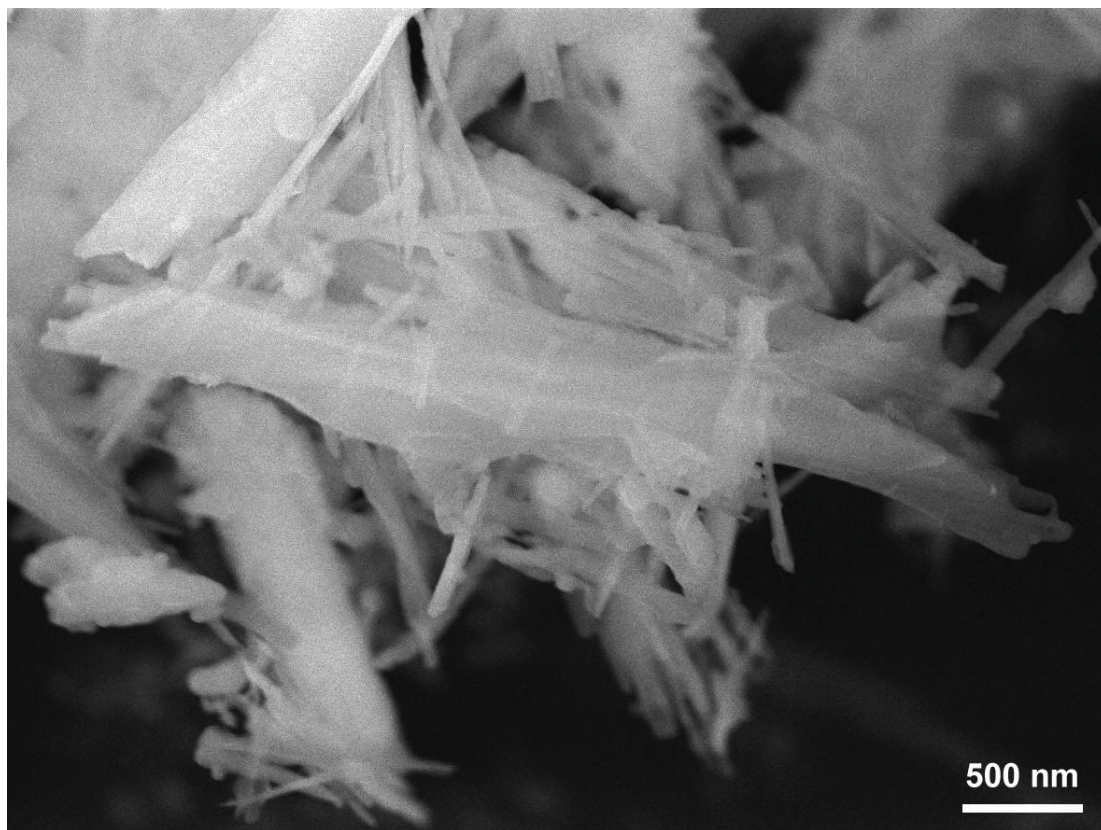
Addition in concrete 3–3.5 mass. % of the fillers based on wollastonite impact frost resistance of the concrete samples obtained increasing the number of freezing-thawing cycles up to 400 (Figure 5). Concrete samples with and without wollastonite additives tested for frost resistance are shown in Figure 6.



**Figure 2:** Dependence of the product yield on the duration of borogypsum autoclave treatment at 220 °C [22]

A promising area of application of the wollastonite obtained is its use in the production of PCM based on UHMWPE. The authors have carried out preliminary studies showing that the addition of wollastonite improves the mechanical and tribotechnical characteristics of the PCM relative to the unfilled UHMWPE. The filling of UHMWPE with wollastonite up to 2 mass. % leads to an increase in the relative elongation at rupture by 18 % and in the tensile strength by 27 % in comparison with the original polymer matrix (Figure 7). Composites containing 20 mass. % wollastonite are also characterized by an increase of elastic modulus by 25 %. Filling UHMWPE with wollastonite increases the wear resistance of composites. The mass wear rate of the polymer composite decreases by 3 times relative to the unfilled UHMWPE. With the increase of wollastonite content from 0.5 to 5 mass. % in UHMWPE, the value of linear wear is observed to be 3 times lower than the original polymer.





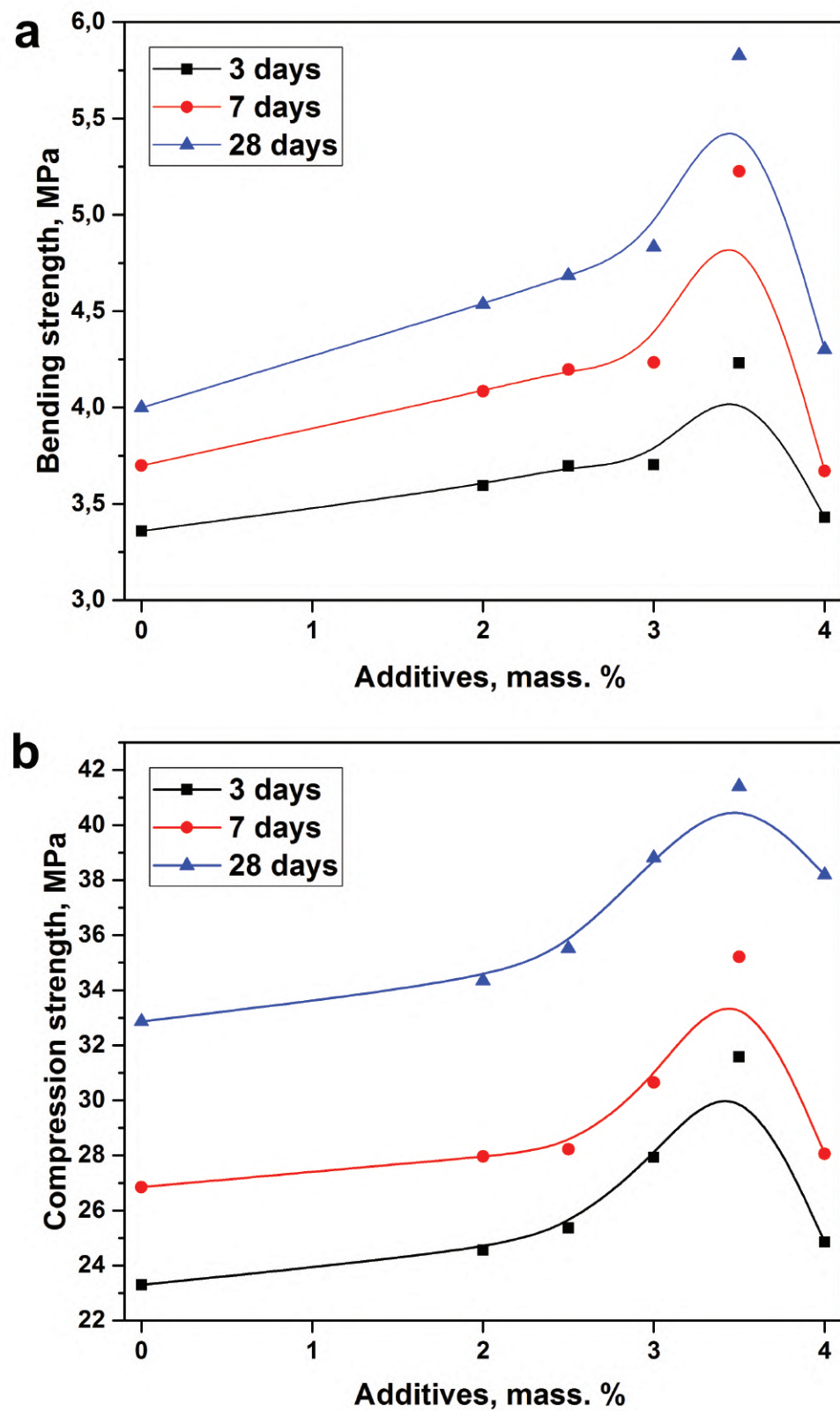
**Figure 3:** SEM images of the microparticles of wollastonite produced by autoclave synthesis at 220 °C [23]

## 4. Conclusion

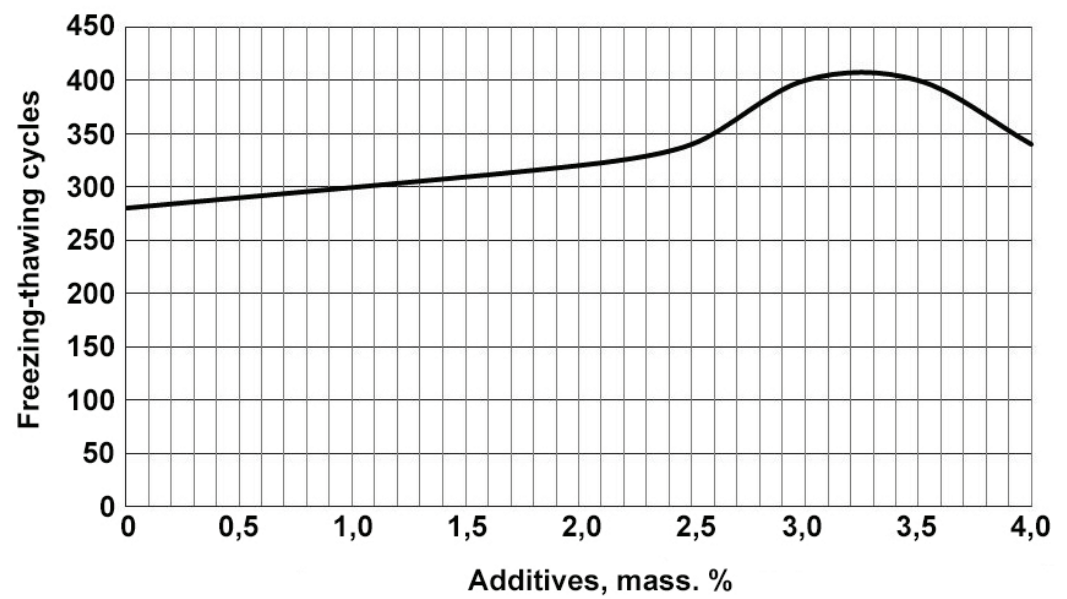
Large quantities of gypsum technogenic waste accumulated in almost every region of the Russian Federation is a potential raw material for synthetic wollastonite and materials based on it. Production set-up of synthetic wollastonite will contribute to the reduction of Russia's demand for wollastonite raw materials while simultaneously solving the problem of multi-tonnage technogenic deposits utilization. On the example of complex processing of boric acid production wastes, it is shown the possibility of obtaining synthetic wollastonite with needle form of particles (depending on synthesis conditions) improving functional characteristics of concretes and polymeric composite materials.

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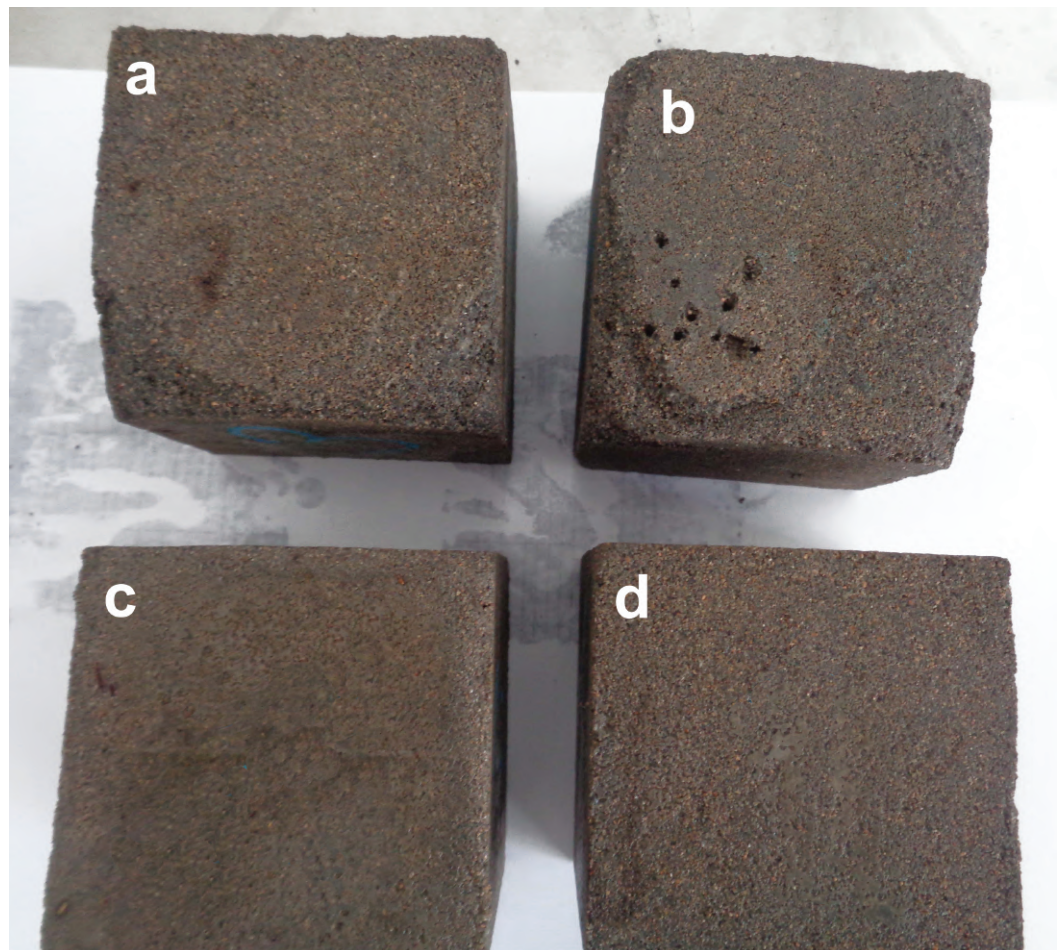




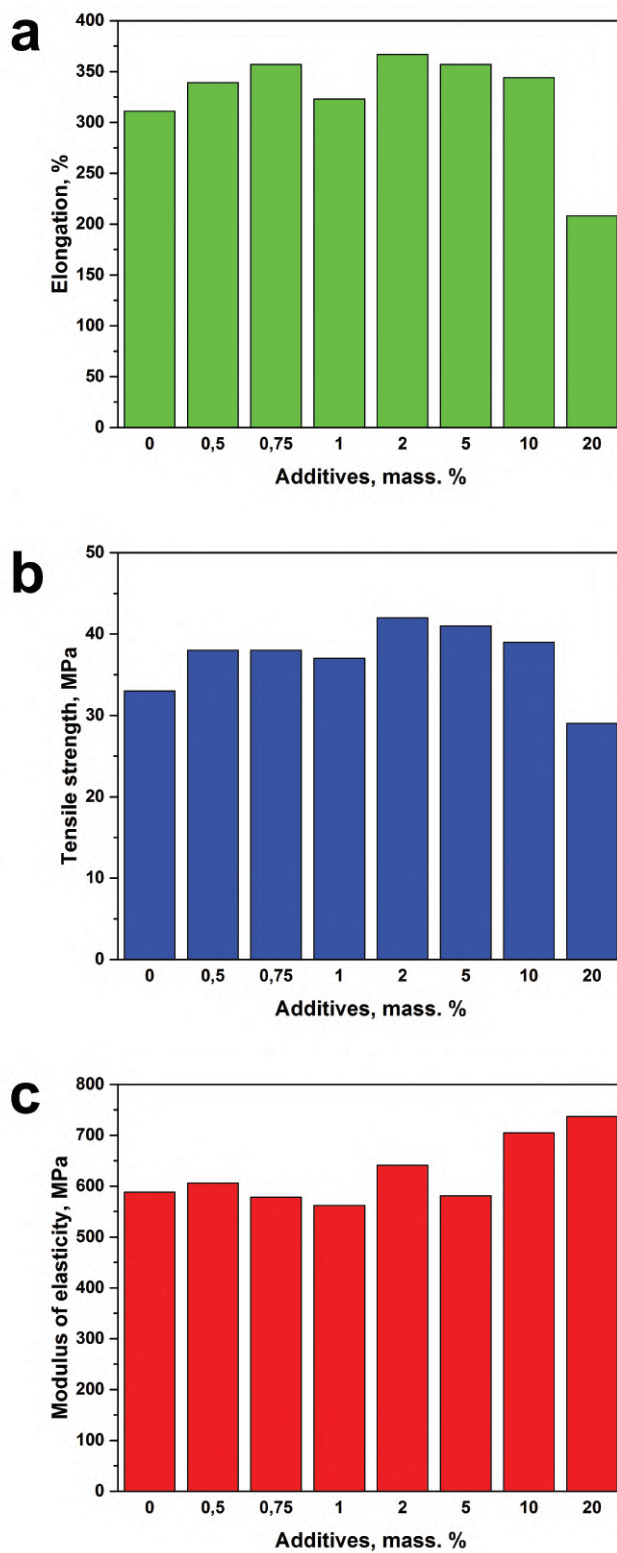
**Figure 4:** The effect of additives based on wollastonite on the strength of fine-grained concrete under bending (a) and compression (b) [26]



**Figure 5:** Impact of the amount of wollastonite added in concrete samples on the number freezing-thawing cycles [26]



**Figure 6:** The samples after frost resistance tests: without wollastonite addition (a, b) and with wollastonite content of 3–3.5 wt. % (c, d)



**Figure 7:** Mechanical properties of PCM with different content of wollastonite: a — elongation, %; b — tensile strength, MPa; c — modulus of elasticity, MPa

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